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Novel Photo-Memory Effect in Photoconductivity of Conducting Polymer Containing Photochromic Dye

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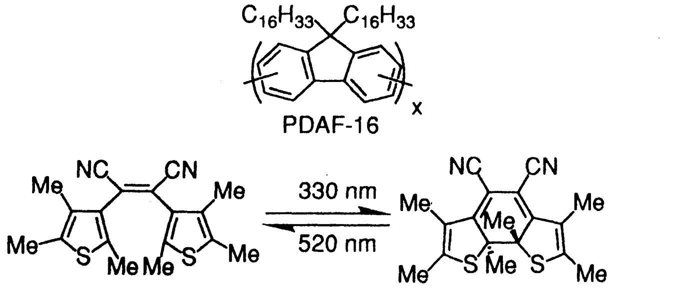
Photoconduction of a conducting polymer, poly(9,9-dihexadecylfluorene) containing a photochromic dye, cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene, is suppressed upon photoisomerization of the dye from ring-open form to ring-closed form but recovered by the reverse photoisomerization. The reversible memory effect in the photoconduction has been discussed on the basis of the energy states of the dye and those trapping effects on the photo-carriers in the conducting polymer.

There has been considerable interest in conducting polymers in recent years. The conducting polymers show reversible insulator-metal transition upon chemical and electrochemical doping. In the doped and photoexcited states, soliton, polaron, and bipolaron are thought to be generated in the conjugated π-electron system, resulting in drastic changes in chemical and physical properties.$^{1)}$ Doping of some functional compounds in the conducting polymers results in drastic changes in the properties of conducting polymers not only in the ground state but also in the photoexcited state when photo-induced charge transfer between the dopant and the π-electron system is possible.$^{2)}$ On the other hand, a number of photochromic compounds have been synthesized and their chemical and physical properties have been studied. Accompanying with the photoisomerization, electronic energy states of the photochromic dye change drastically resulting in the photochromism. Some functional applications of the photochromic compounds have also been proposed utilizing photo-induced changes in ionic conductivity of electrolyte, in solubility of polymers, in volume of gel, etc.$^{3,4)}$

In the present study, effects of incorporation of a photochromic dye on the electrical properties of a conducting polymer are investigated and a novel photo-memory effect is demonstrated. The conducting polymer used here is poly(9,9-dihexadecylfluorene) (PDAF-16), shown in Fig. 1, which is soluble in various organic solvents.$^{5)}$ The used photochromic dopant is cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (CMTE). Irie etal. have recently reported synthesis and properties of CMTE which shows photoisomerization behaviour upon irradiation of UV-light (ca. 330 nm) and Vis-light (ca. 520 nm) as also illustrated in Fig. 1 and has excellent thermal stability both in the



CMTE; ring-open (yellow) form

CMTE; ring-closed (red) form

Fig. 1. Structure of PDAF-16 and schematic illustration of photoisomerization of CMTE.

ring-open (yellow) and the ring-closed (red) forms.[6) PDAF-16 and the red form CMTE have Vis-absorption peaks at around 380 nm and 520 nm, respectively, while the yellow form CMTE has UV-absorption peak at 330 nm.

PDAF-16 and CMTE were synthesized and purified by the previously reported method.[5,6) CMTE-PDAF-16 composite was prepared by mixing PDAF-16 and the yellow form CMTE in chloroform solution and casting the solution on an appropriate substrate. For the photoconduction measurements, the cast film of CMTE/PDAF-16 was held between two glass or quartz plates coated with ITO (In-Sn-Oxide) layer. A xenon lamp (350 W) was used as an irradiation light source in the photoconduction experiments and also in the measurements of effects of light irradiation. The excitation light in the photoconduction measurements was irradiated through the anode ITO layer.

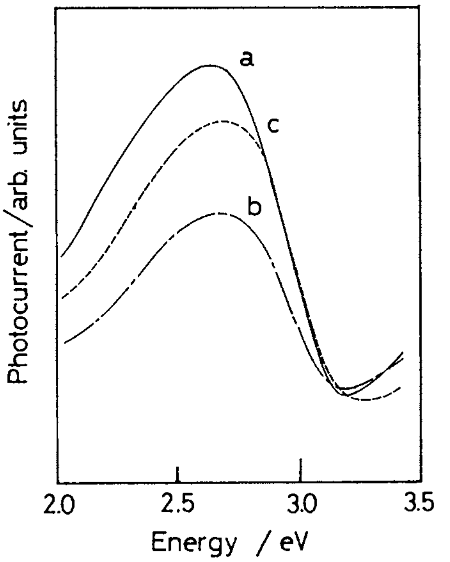


Fig. 2. Photoconduction spectra of PDAF-16 doped with 10% of CMTE (a) initial, (b) after irradiation of 340 nm , (c) after irradiation of 520 nm after measurement of (b).

As indicated in Fig. 2 (a), the CMTE-PDAF-16 composite showed clear photoconduction peak at energy slightly lower than the band gap energy of PDAF-16. The photoconduction current of the CMTE-PDAF-16 composite was smaller than that of pure PDAF-16 while peak energy and peak shape were not influenced by incorporation of CMTE, indicating a quenching effect of the dye. Photoluminescence measurements of PDAF-16 also showed the quenching effect of CMTE. Since there was no photoconduction peak corresponds to excitation of CMTE, excitation of CMTE molecules is thought to give no remarkable direct contribution to the photoconduction behaviour.

Upon irradiation of the UV-light of 340 nm in wavelength, the photoconduction peak was suppressed, while the peak energy and the shape were not varied remarkably. In these experiments, the monochromatic xenon light of 340 nm was irradiated upon the sample ahead the photoconduction measurements. As evident in curve (b) in Fig. 2, the photoconduction was suppressed upon pre-irradiation of 340 nm light. Since these experiments were performed under vacuum and the non-doped sample showed no marked light irradiation effect, the decrease in the photoconduction signal is thought to be originated from effects of the photochromic dye and not from any effect of oxygen and moisture. Moreover, the photoconduction signal was enhanced by pre-irradiation of monochromatic light of 520 nm from curve (b) to curve (c) in Fig. 2, while the peak energy and shape showed no marked change. The resultant photoconduction spectrum and intensity obtained after pre-irradiation of the green light as long as 1 h is just same as those of original non-irradiated sample. The photoconduction of the CMTE-PDAF-16 composite film was, therefore, suppressed upon pre-irradiation of 340 nm light and the original signal can be recovered by the pre-irradiation of 520 nm light. These changes in the photoconduction signal were reversible and showed clear reproducibility.

These photoirradiation effects can be explained in terms of photoisomerization effect of CMTE. Change in absorption spectrum of the test sample upon photoirradiations was investigated. As shown in Fig. 3, novel absorption peak appeared at 540 nm after pre-irradiation of 340 nm light while the absorption peak at 380 nm corresponding to the band gap transition of PDAF-16 showed no marked change, indicating occurrence of photoisomerization of CMTE from the yellow form to the red form even in the polymer layer. Judging from the peak intensity at 540 nm of Fig. 3, the ratio of amounts of the red form molecules seems to be as high as that in the case of photochromism observed in organic solvents such as hexane. Upon irradiation of 340 nm light, absorption spectrum of CMTE solution and its solid film showed clear change and estimated HOMO-LUMO energy gap decreased from 2.8 eV to 2.0 eV, corresponding to photoisomerization of CMTE from the yellow form to the red form as shown in Fig. 1.

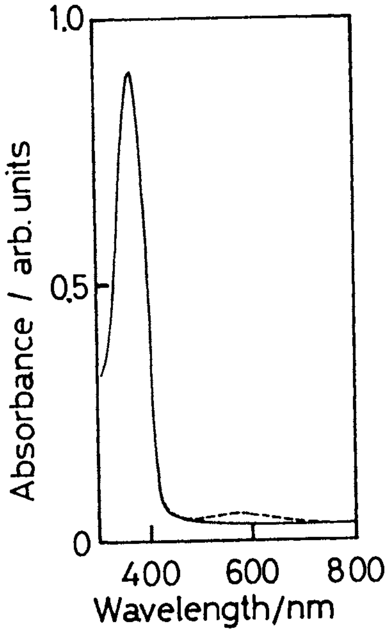


Fig. 3 Absorption spectra of PDAF-16 doped with CMTE after photoirradiation of 340 nm (a) and 540 nm (b).

Figure 4 shows cyclic voltammograms of an ITO(In-Sn-Oxide) electrode immersed in 1 mmol cm^{-3} of CMTE/acetonitrile solution containing 0.1 mol cm^{-3} TBAFB (tetrabutyl ammonium fluoroborate) as a supporting electrolyte. In this experiment, the CMTE sample was in yellow form in the initial state. There was no marked oxidation current at electrode potential lower than 1.4 V vs. Ag in the as-prepared solution and after the Vis-light irradiation (540 nm). However, after the UV-light irradiation of 340 nm, a clear oxidation current wave was observed at 0.8V vs. Ag. Since no marked oxidation current wave was observed below 2.0 V vs. Ag in the blank solution, these oxidation current waves indicate oxidation of each isomer of CMTE. Upon these oxidation of CMTEs, cation radicals of CMTEs might be formed by removing an electron from the HOMO states.

From the oxidation potentials and the HOMO-LUMO gap energies, relative energy levels of HOMO and LUMO of each isomer of CMTE can be evaluated as illustrated in Fig. 5 by neglecting effects of electrolyte solvent and salt on the oxidation potentials of CMTEs. Figure 5 also shows relative energies of electronic states of PDAF-16 which were evaluated from the previous results.[7] Though origin of the slight shift in the photoconduction peak shown in Fig. 2 is not clear at this stage, the photoirradiation effects on the photoconduction intensity can be explained in terms of photo-induced changes in electronic properties of CMTE as follws. The changes in the photoconduction response upon photoisomerization might be explained by taking trapping effect of the CMTEs on the photo-generated positive charge carriers, since the positive charge carriers seems to be the dominate carriers in the conducting polymer[8] and the photoconduction spectra were measured by irradiating the excitation light through the positive ITO electrode. As evident in Fig. 5, the HOMO states of the both CMTEs are higher than the top of valence band of PDAF-16 in energy. However, the difference in energy

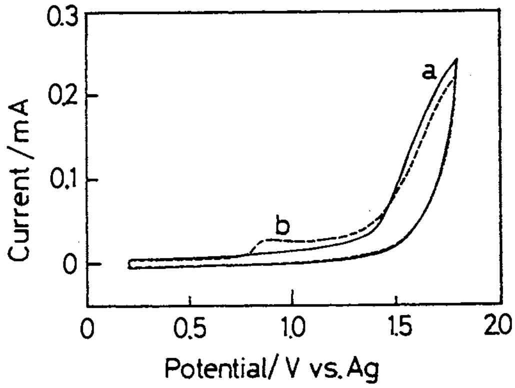


Fig. 4. Change in cyclic voltammogram of ITO electrode in 1 mmol dm^{-3} CMTE/acetonitrile solution containing 0.1 mol dm^{-3} TBAFB. (a) after irradiation of 340 nm, (b) after irradiation of 520 nm.

is larger in the red form in comparison with that in the yellow form. Therefore, the photo-generated positive charge carriers on the valence band of PDAF-16 seem to be trapped effectively by the HOMO state of the red form CMTE, while weakly by that of the yellow form. Larger difference between trapping effects of the red and the yellow form CMTEs is expected on the photo-generated positive polaron state taking energy of the polaron state of PDAF-16. The photoluminescence peak energy of PDAF-16 is found to be 2.3 eV in energy which suggests that position of the polaron state of the PDAF-16 is 0.3 - 0.4 eV higher in energy than the top of valence band. This estimated energy of the polaron state is in good agreement with the previous resultconcerning on electrochromism of a derivative of PDAF-16[9] and suggests that the photo-generated polaron should be trapped by the HOMO state of the red form CMTE and not by that of the yellow form CMTE. These changes in properties of photo-induced charge transfer between the conducting polymer and the photochromic dye are thought to result in the change in photoconduction upon light irradiation.

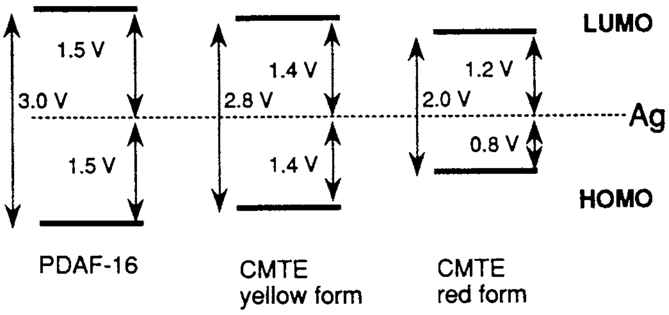


Fig. 5. Energy states of PDAF-16 and CMTE of the red form and the yellow form.

In conclusion, photoconduction of CMTE-PDAF-16 composite can be controlled reversibly with light irradiation of 340 nm and 540 nm. The red form CMTE results in smaller photoconduction response than the yellow form CMTE. This photoisomerization effect on the photoconduction behaviour of PDAF-16 was explained from change in the HOMO state of CMTE upon photoisomerization and also change in the trapping probability of the photo-charge carriers generated on the π-electron system of PDAF-16 by the HOMO states of CMTEs. These photoirradiation effects of photochromic dye-conducting polymer composite are possible to use in a photo-memory or other photo-functional applications. Cycling behaviour and optimization of various conditions such as temperature, doping ratio, alkyl chain length of PDAF, kind of photochromic dye, and reading and writing wavelength are still on study as well as the detailed mechanism of the photo-memory effect.

References

1) E. S. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett., **42**, 1698 (1979).
2) K. Yoshino, X. H. Yin, S. Morita, T. Kawai, and A. A. Zakhidov, Chem. Express, **7**, 817(1992).
3) M. Irie, "Denshi Hikari Kinousei Koubunshi", (Electro- and Photo-Functional Polymers), ed. by K. Yoshino, Kohdansyasaientifikku, Tokyo(1991), p.95.
4) K. Yokoyama, T. Yamashita, and M. Yokoyama, Chem. Lett., **1991**, 965.
5) M. Fukuda, K. Sawada, and K. Yoshino, Jpn. J. Appl. Phys., **28**, L1433 (1989).
6) M. Irie and M. Mohri, J. Org. Chem., **53**, 803 (1988).
7) M. Fukuda, K. Sawada, S. Morita, and K. Yoshino, Synth. Met., **41-43**, 855 (1991).
8) Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, Jpn. J. Appl. Phys., **30**, L1941 (1991).
9) J. R. Berthelot, V. Questaigne, J. Simonet, and G. Peslerbe, New. J. Chem., **13**, 45 (1989).

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